



Catalytic combustion of chlorobenzene over Ru-doped ceria catalysts: Mechanism study

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ABSTRACT

To investigate the mechanism of the catalytic combustion of chlorobenzene over pure CeO₂ and Ru doped CeO₂ catalysts, we examined the oxidation reaction in depth by temperature-programmed surface reaction (TPSR) technique and a series of supplementary experiments. The results suggest that the C–Cl bond in chlorobenzene molecule can be dissociated easily on Ce³⁺/Ce⁴⁺ active sites, and the dissociated chlorobenzene can be rapidly oxidized into CO₂ and H₂O by surface reactive oxygen or lattice oxygen. The chlorine species dissociatively adsorbed on the active sites can result in the rapid deactivation of catalysts and be removed in form of Cl₂ via the Deacon Reaction catalyzed by RuO₂ or CeO₂, which would improve the catalyst stability. Additionally, the partial chlorination of RuO₂ or CeO₂ possibly occurs during the long reaction, which is responsible for the production of dichlorobenzene by-products.

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1. Introduction

The catalytic oxidation and combustion of chlorobenzene (CB) has been widely studied as model reactions of dioxin combustion in waste gases or municipal solid wastes treatments, due to chlorobenzene known to be an important precursor of dioxin (such as polychlorinated dioxins (PCDDs) and dibenzofuranes (PCDFs)) and its high toxicity and delicate manipulation in laboratories. Catalytic combustion of chlorobenzene is generally carried out over three main catalyst types: Vanadia-based catalysts, such as V₂O₅–TiO₂ [1], V₂O₅–WO₃–TiO₂ [2], V₂O₅–MoO₃–TiO₂ [3], noble metals (Pt, Pd) supported on various oxides [4] and zeolites [5]. However, these catalysts often present some problems, such as relative low activity, rapid deactivation by chlorine poisoning or coking, high cost, or the formation of undesired polychlorinated benzenes. In our previous works [6–8], it was found that CeO₂ and transition metals (such as Fe, Co, Cu, Ni and Mn) doped CeO₂ catalysts present high activity and better stability for catalytic oxidation of various chlorinated hydrocarbons (CHCs), such as chlorobenzene, dichloroethane (DCE) and trichloroethylene (TCE). Additionally, Zhou and Gutiérrez-Ortiz et al. also achieved very significant and outstanding results in this field [9–11]. These

researches showed that the CeO₂ based catalysts are suitable and promising for catalytic combustion of CHCs.

Recently, we reported that Ru doped CeO₂ catalysts show high activity and stability at low temperature (275 °C) for the catalytic combustion of CB [12]. However, there are still many details to further study. Thus, the aim of this work is to further investigate the performance and possible reaction mechanism of Ru doped CeO₂ catalysts toward the catalytic oxidation of chlorobenzene by TPSR technique. Furthermore, the effect of water on catalytic activity and intermediate-product formation was carried out.

2. Experimental

2.1. Catalysts preparation

Pure CeO₂ and 1%Ru doped CeO₂ catalysts were synthesized by a simple precipitation/co-precipitation method using NaOH as the precipitating agent and 1%Ru/SBA-15 as reference catalyst was prepared by incipient-wetness impregnation method, and for more detailed procedures see Ref. [12].

2.2. Catalysts characterization

XRF, XRD, N₂ adsorption, TEM/HRTEM, Raman, XPS and H₂-TPR were used to investigate the physico-chemical properties of the catalysts. The actual content of Ru in 1%Ru–CeO₂ and 1%Ru/SBA-15 catalysts measured by XRF is 0.58% and 0.98%, and the surface area

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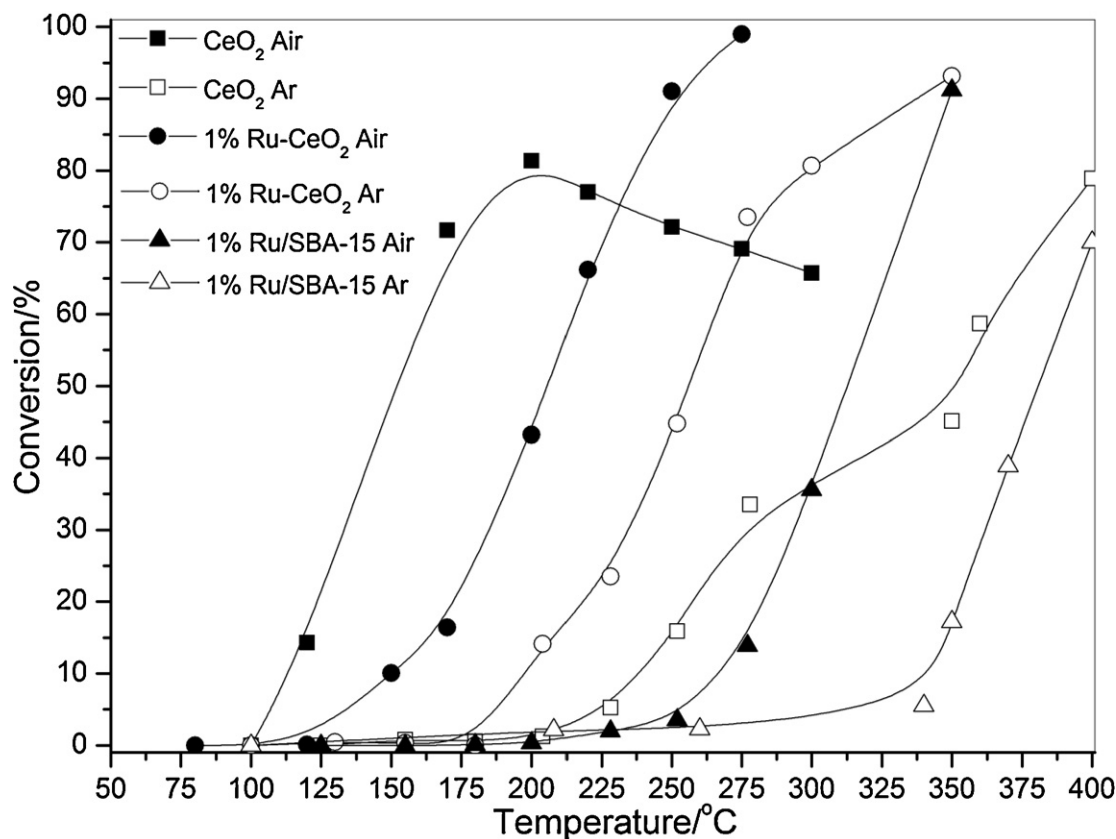


Fig. 1. Conversion of chlorobenzene over pure CeO_2 , 1%Ru- CeO_2 and 1%Ru/SBA-15 catalysts in absence and presence of O_2 . CB concentration: 550 ppm; GHSV: 15,000 h^{-1} ; catalyst amount: 200 mg.

of pure CeO_2 , 1%Ru- CeO_2 and 1%Ru/SBA-15 is 100.8, 105 and 452 $\text{m}^2 \text{g}^{-1}$, respectively. For the other detailed results see Ref. [12].

2.3. Catalytic activity measurement

Catalytic combustion reactions were carried out in a continuous flow microreactor constituted of a U-shaped quartz tube of 3 mm of inner diameter at atmospheric pressure. 200 mg catalysts were placed at the bottom of the microreactor. The feed flow through the reactor was set at 40 $\text{cm}^3 \text{min}^{-1}$ and the gas hourly space velocity (GHSV) was maintained at 15,000 h^{-1} . Feed stream to the reactor was prepared by delivering liquid CB with a syringe pump into dry air and the injection point was electrically heated to ensure complete evaporation of the liquid reaction feeds. The concentration of CB in the reaction feeds was set at 550 ppm. The water vapour fed into the system was made by bubbling air into water in a temperature-controlled saturation system (25 °C). In order to minimize the possible adsorption of the CB on the inner surface of piping, the piping was heated ($T = 100^\circ\text{C}$) by a heater band. The temperature of the reactor was measured with a thermocouple located just at the bottom of the microreactor and the effluent gases were analyzed by an on-line gas chromatograph equipped with a FID detector. Catalytic activity was measured over the range 100–400 °C and conversion data were calculated by the difference between inlet and outlet concentrations. Conversion measurements and product profiles were taken after maintained for 5 min at each test temperature. Additionally, mass spectrometry was used for the determination of the main intermediates and by-products.

The TPSR measurement was carried out in the same equipment as the catalytic activity tests. First, the Ar containing a certain concentration (such as 1500 ppm) of CB or the mixture of CB and

benzene (B) flowed continuously the catalysts at 100 °C. After the adsorption–desorption reached an equilibrium (the concentration of CB or B in the effluent gas is monitored by a gas chromatography), the catalysts were heated from 100 °C to a specified temperature (300 °C or 400 °C) at 10 °C min^{-1} . After maintained for a period of time at this temperature to achieve the complete or partial deactivation of catalysts, a certain amount of O_2 was admitted into the feed stream and the content of oxygen was set at 10% (v/v). The reactant and the products (such as CB ($m/z = 112$), CO_2 (44), CO (28), Cl_2 (70), HCl (36), dichlorobenzene (146), and B (78)) were analyzed on-line over a mass spectrometer apparatus (HIDEN QIC-20).

3. Results and discussion

3.1. The effect of gaseous oxygen

For the catalytic combustion or total oxidation of non-chlorinated volatile organic compounds (VOCs), the gaseous oxygen is essential and the main role is to replenish the consumed surface active oxygen or lattice oxygen as an oxidizing agent, or directly as a reactant (namely oxidizing agent). However, for the catalytic combustion of chlorinated hydrocarbons, the role of oxygen besides acting as an oxidizing agent also includes: resisting chlorine poisoning, forming a new active phase during reaction, and determining the distribution of products or by-products. For examples, Louw et al. [13] demonstrated that the oxygen concentration influence the catalyst performance and the formation of MeO_xCl_y species for CB catalytic combustion over noble metals catalysts, and which play a important role in the formation of polychlorinated benzenes. Li et al. [14] found that the active phase of the $\text{MnO}_x/\text{TiO}_2$ catalysts was mainly oxychlorinated manganese (MnO_xCl_y) owing to the excess of O_2 , the catalyst cannot be fully chlorinated. In our

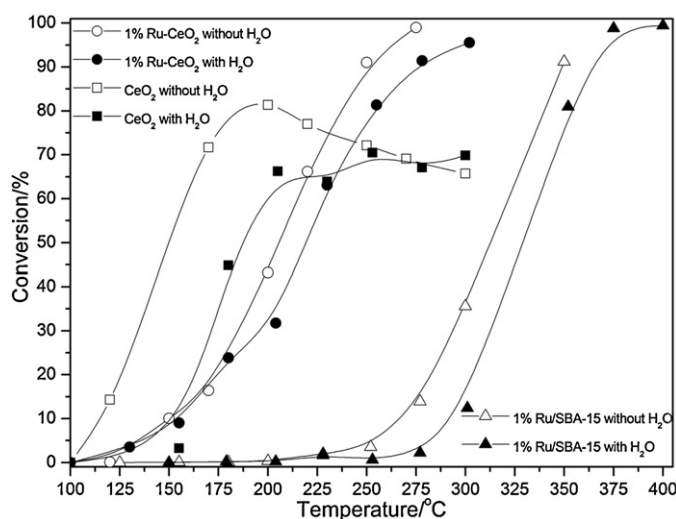


Fig. 2. Conversion of chlorobenzene over 1%Ru-CeO₂, 1%Ru/SBA-15 and CeO₂ catalysts under dry and water (~3%, v/v) air conditions. CB concentration: 550 ppm; GHSV: 15,000 h⁻¹; catalyst amount: 200 mg.

previous works [15], it was found that 1,2-DCE and TCE can be oxidized to CO₂ besides a small amount of C₂H₂Cl and C₂HCl in absence of gaseous oxygen over CeO₂ and MnO_x-CeO₂ catalyst. Dai et al. [16] investigated the effect of oxygen concentration [O₂] on the activity for catalytic combustion of chlorobenzene over Mn-Ce-La-O mixed oxide catalysts, and the results showed that the effect of [O₂] on the activity was not significant, especially at lower 250 °C. Accordingly, it is important to thoroughly know the influence of O₂ on the CeO₂ based catalysts performance and understand the mechanism of CB catalytic combustion.

Fig. 1 presents the conversion of chlorobenzene catalytic combustion on 1%Ru-CeO₂, 1%Ru/SBA-15 and CeO₂ catalysts in absence and presence of O₂. The results showed that all the catalysts demonstrate evident activity in absence of O₂ although the activity was much lower than that in presence of O₂, especially T_{50%} and T_{90%} of 1%Ru-CeO₂ catalyst only 260 °C and 335 °C, respectively. Compared with 1%Ru-CeO₂ catalyst, the decrease of catalytic activity of the pure CeO₂ in absence of O₂ is more significant, and the T_{50%} increases from 150 °C to 350 °C. Additionally, the MS results (Fig. 3) show the main products containing carbon over 1%Ru-CeO₂ and CeO₂ catalysts are CO₂ and benzene (B), and no CO is observed. However, on 1%Ru/SBA-15, a small amount of CO and only trace amount of benzene are detected. It is generally acknowledged that the splitting of the first C–Cl bond is the rate controlling step for the catalytic decomposition of chlorinated hydrocarbons, and then the CH_x species are easily oxidized by active oxygen species such as adsorbed surface oxygen. As we all know, ceria has found its primary utilization in catalysis as an oxygen carrier due to its high oxygen storage capacity (OSC), which uptake and release oxygen via the transformation between Ce³⁺ and Ce⁴⁺. Furthermore, the O₂-TPD profiles (Fig. S1) show the evolution of O₂ under Ar atmosphere and two O₂ desorption peaks at 130 °C and 425–475 °C are observed, and the 1%Ru-CeO₂ presents lower desorption temperature and higher amount of O₂ in high temperature range comparing with CeO₂ catalysts (H₂-TPR also demonstrated similar results [12]). The former is attributed to the physically adsorbed oxygen species and the latter is corresponded to chemically adsorbed surface oxygen species or the evolution of lattice oxygen. Thus, in absence of gaseous O₂, the dissociated chlorobenzene (phenyl groups) still can be oxidized into CO₂ by the surface or lattice oxygen species from CeO₂ based catalysts, and 1%Ru-CeO₂ catalyst presents higher catalytic activity. Additionally, it can be found that the color of CeO₂ catalyst changed from yellow (CeO₂) to blue

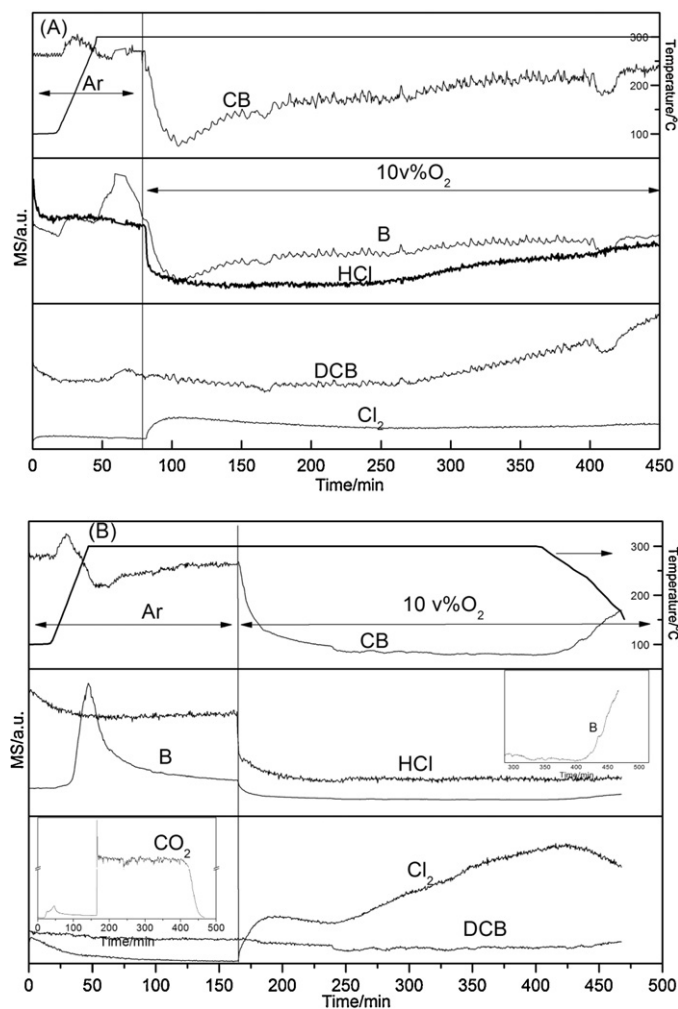


Fig. 3. TPRS profiles for CB decomposition over CeO₂ (A) and 1%Ru-CeO₂ (B) catalysts at 300 °C. CB concentration: 1500 ppm; GHSV: 15,000 h⁻¹; catalyst amount: 200 mg.

(Ce₂O₃) (see Fig. S2) after the activity test, which indicated that the lattice oxygen of CeO₂ was consumed and the formation of Ce₂O₃.

3.2. The effect of H₂O

Generally, the CHCs in industry waste gases co-exist with water, moreover, water is also used as a hydrogen source to increase the HCl yield [17]. Therefore, the effect of water in the feed on the conversion of CB was investigated and the results were shown in Fig. 2. With addition of 3% (by volume of reactant gas) water into the air containing CB, the activity of CB over all catalysts is significantly reduced, especially pure CeO₂ catalyst. This inhibition by water probably reflects the competition of the reactant molecules with water molecules for adsorption on the active sites (such as oxidation active sites). The theoretical prediction [18] and experiments [19] both indicated that water should bind preferentially to oxygen vacancy sites and the dissociated OH group easily fills the oxygen vacancy. Our previous studies [15] indicated that the catalytic decomposition of CHCs over CeO₂ based catalysts was related with the concentration of oxygen vacancies, which is the main active site adsorbing and oxidizing the dissociated CHCs. Additionally, the effect of water on the CB conversion and selectivity to benzene in absence of oxygen would be discussed detailedly in the later section.

3.3. The effect of Deacon Reaction on the stability of CeO₂ based catalysts

Fig. 3 describes the catalytic decomposition of CB over CeO₂ and 1%Ru-CeO₂ under Ar or O₂ (10 vol.%) / Ar atmosphere by an online MS. Over these two samples, a desorption peak of CB can be observed between 130 and 250 °C, meanwhile, the decomposition of CB also was monitored especially above 180 °C (the formation of CO₂ was monitored by MS, see Fig. 3B(inset)). With the increase of reaction temperature, the conversion of CB rapidly increases and the conversion over 1%Ru-CeO₂ catalyst is significantly higher than that over CeO₂ catalyst, which is consistent with the results in activity test (Fig. 1). Additionally, it can be found that the pure CeO₂ catalyst showed poor stability and the complete deactivation was observed within 30 min at 300 °C under Ar atmosphere (confirmed by gas chromatography). By contrast, the 1%Ru-CeO₂ catalyst still presented visible catalytic activity within 100 min. The rapid deactivation of CeO₂ based catalysts under Ar condition can be ascribed to the two reasons presented below: (1) the adsorption of inorganic chlorine species (dissociative Cl) on active sites or surface; (2) the complete consumption of oxygen species (including surface and lattice oxygen). Compared with pure CeO₂, the lattice oxygen of 1%Ru-CeO₂ catalyst possesses the higher mobility and the more evolution amount, and thus 1%Ru-CeO₂ catalyst can show a better stability under Ar atmosphere. Moreover, the formation of the by-product benzene is observed, which comes from the incomplete oxidation of CB due to the absence of active oxygen species with strong oxidizing ability.

Subsequently, O₂ (4 mL) is admitted into the reaction feed; it can be found that the conversion of CB over pure CeO₂ and 1%Ru-CeO₂ catalysts both shows a rapid increase and a large amount of CO₂ also is detected, but the spent time reaching the maximum conversion is different and the pure CeO₂ is more faster than 1%Ru-CeO₂ catalyst (there exists an induction period to obtain the highest activity, which is consistent with our previous results [12]). Moreover, the rapid deactivation of pure CeO₂ is observed, while 1%Ru-CeO₂ catalyst presents a better stability (the evident deactivation is not observed during the whole test). Additionally, the formation of HCl and Cl₂ is monitored by online MS. The change of HCl is almost negligible over pure CeO₂ and 1%Ru-CeO₂ catalysts after O₂ is admitted into the feed, which may result from the lower content of HCl or the lower sensitivity of MS to HCl. However, it is worth noting that the monitoring result of Cl₂ over these two catalysts reveals significant differences. The amount of Cl₂ over 1%Ru-CeO₂ catalyst continuously increases with reaction time, especially after the induction period (after about 70 min), but the formation of Cl₂ over pure CeO₂ catalyst is not observed except during the initial reaction. Obviously, the inorganic chlorine species from the decomposition of CB can be removed from the catalyst surface in the form of Cl₂ over 1%Ru-CeO₂ catalyst, which attributes to the Deacon Reaction catalyzed by Ru (Ru-based catalyst shows very high reactivity for the oxidation of HCl and easier Cl₂ evolution [20,21]). Additionally, the by-products dichlorobenzene (DCB, mainly includes 1,4-DCB and 1,2-DCB, confirmed by GC) can be observed over pure CeO₂ catalysts after at least 2 h, but no DCB over 1%Ru-CeO₂ catalyst (actually, the concentration measured by gas chromatography is lower than 10 ppm, see Fig. S3, which may be below the lower limit of MS), which is possible ascribed to the partially chlorinated RuO₂ or CeO₂. Moreover, the by-products B and DCB can be detected over 1%Ru-CeO₂ catalyst during the cooling period. Combined with our previous results, it can be confirmed that the removal of the Cl dissociatively adsorbed on the active sites is crucial to improve the stability of CeO₂ based catalysts, and the oxidation of these dissociatively adsorbed Cl into molecule chlorine (Cl₂) via Deacon Reaction may be a suitable solution.

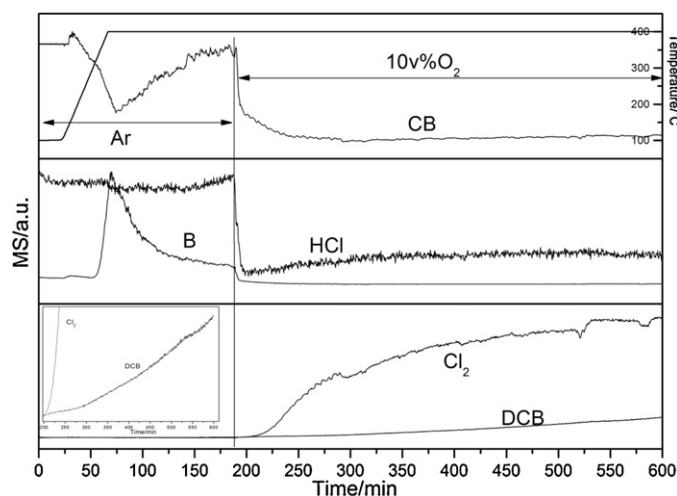


Fig. 4. TPSR profiles for CB decomposition over CeO₂ catalyst at 400 °C. CB concentration: 1500 ppm; GHSV: 15,000 h⁻¹; catalyst amount: 200 mg.

Recently, some studies [22–24] indicated that CeO₂ presents remarkable catalytic activity for the HCl oxidation to Cl₂ and has excellent stability at high temperature. However, the oxidation reaction over pure CeO₂ catalyst generally is carried at higher temperature (such as 400–450 °C) compared with Ru based catalysts, and at least above 350 °C. According to these results, it can be speculated that the pure CeO₂ catalyst would demonstrate a better stability for the CB catalytic combustion at higher temperature (such as 400 °C) if the opinion that the stability of CeO₂ catalysts can be improved by Deacon Reaction is correct. Thus, the stability of CeO₂ catalyst at 400 °C was investigated by TPSR method and presented in the Fig. 4.

Fig. 4 shows TPSR profiles for CB decomposition over pure CeO₂ catalyst at 400 °C. Under Ar condition, the formation of by-product B and the rapid deactivation of CeO₂ catalyst are observed. After oxygen is admitted into the reaction system, the catalytic activity of the deactivated CeO₂ catalyst can be recovered instantly, which is consistent with the results at 300 °C. However, the formation of Cl₂ is obviously detected after 15 min and increases with the increase of reaction time, and then tends gradually to a constant value with 400 min. Simultaneously, the by-products DCB (including 1,4-DCB and 1,2-DCB, confirmed by GC) also is monitored accompanied with the formation of Cl₂. Not surprisingly, the pure CeO₂ catalyst shows a good stability for the CB catalytic combustion at 400 °C within 400 min.

In order to further confirm the stability of the pure CeO₂ catalyst, the stability and by-products of CeO₂ catalyst for CB catalytic combustion were investigated at different temperature via the activity tests method and the results were presented in Fig. 5. It can be found that the conversion of CB over the CeO₂ catalyst at 400 °C always maintains at 95% within 30 h and the deactivation is not observed (see Fig. 5(A)), but the conversion sharply drops from 82% to 0% within 3.5 h at 300 °C (see Fig. 5(B)). Additionally, the main by-products 1,4-DCB and 1,2-DCB are detected and the concentration are about 50–70 ppm, which probably results from the partial chlorination of CeO₂ surface and the formation of Lewis acid. Moreover, Fig. 5(B) further indicates that the CeO₂ catalyst still shows good stability at 400 °C even at high GHSV (60,000 h⁻¹) and the conversion of CB can be stabilized at about 62%. According to Fig. 4 and Fig. 5, it can be concluded that the stability of the pure CeO₂ catalyst for the CB catalytic combustion at higher temperature (such as above 400 °C) is confirmed, which attributes to the catalytic activity of CeO₂ for the oxidation of the Cl dissociatively adsorbed on the

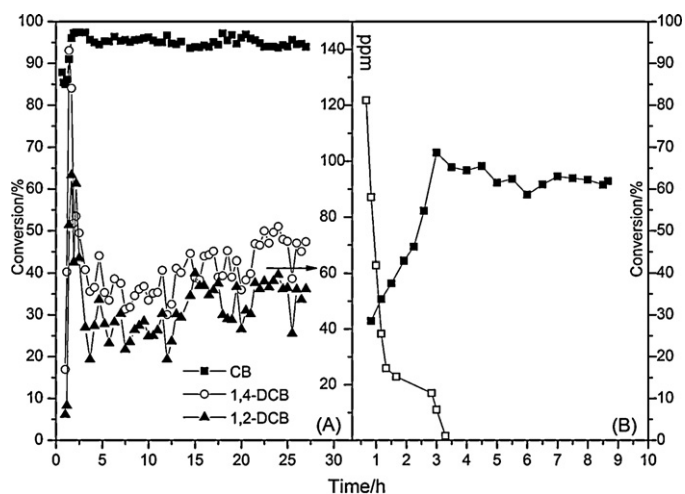


Fig. 5. The stability and distribution of chlorinated products over CeO_2 catalyst for CB catalytic combustion: (A) at 400 °C; CB concentration: 1500 ppm; GHSV: 15,000 h^{-1} ; (B) (□) at 300 °C; CB concentration: 1500 ppm; GHSV: 15,000 h^{-1} ; (■) at 400 °C; CB concentration: 1,500 ppm; GHSV: 60,000 h^{-1} .

active sites into Cl_2 and the rapid removal of the inorganic chlorine species in the form of Cl_2 from catalyst surface.

3.4. The dissociation of C–Cl bond and the formation of benzene

During catalytic activity tests (Fig. 1) and TPSR experiments (Fig. 3), the byproduct benzene both could be found over 1%Ru- CeO_2 and CeO_2 catalysts under Ar atmosphere, but no benzene was observed in the presence of gaseous oxygen. As we all know, the formation of benzene via chlorobenzene generally should include two steps: dechlorination and hydrogenation. The dechlorination of CB (the splitting of C–Cl bond) easily due to the bond dissociation energies (BDE) for C–Cl (399.6 kJ mol^{-1}) is lower than that of C–H bonds (about 462 kJ mol^{-1}), and mainly carries on the $\text{Ce}^{4+}/\text{Ce}^{3+}$ [15]. However, the necessary hydrogen source for the hydrogenation step is absent in the reaction system. It is speculated that the hydroxyl groups adsorbed on CeO_2 surface is a main hydrogen source [25,26], and the water from the CB decomposition maybe another hydrogen source, due to water can be dissociated into two hydroxyl groups on the CeO_2 surface: the OH fragment from water adsorbed on the Ce site (OH_{ads}) and the H fragment adsorbed on one of the surface oxygen (O_s) sites forming the $\text{O}_s\text{H}_{\text{ads}}$ group [18,27]. Additionally, ceria-supported, precious-metal catalysts are one class of materials that have been identified as exhibiting very interesting properties for the water-gas-shift (WGS) reaction ($\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$) with fuel cells to generate H_2 [28–30], due to H_2O can be easily dissociated into H_{ad} and OH_{ads} over CeO_2 or reduced directly to H_2 ($\text{H}_2\text{O} + \text{Ce}_2\text{O}_3 \rightarrow 2\text{CeO}_2 + \text{H}_2$). Therefore, the effect of water on the formation of benzene under Ar atmosphere is investigated and the results are presented in Fig. 6.

Fig. 6(A) shows the conversion of CB under dry and water (~3%, v/v) conditions and in the absence of gaseous oxygen. Pure CeO_2 and 1%Ru- CeO_2 catalysts demonstrate a similar result with that in the presence of gaseous oxygen, the presence of water inhibits evidently the catalytic activity and the decrease of CeO_2 catalyst activity is more significant. However, 1%Ru/SBA-15 catalyst shows a better catalytic activity under humid condition. It is considered that the oxidation is the major pathway for CB destruction over the CeO_2 based catalysts at the conditions of our study due to the abundant surface oxygen species on the CeO_2 and the easier migration of lattice oxygen, whereas hydrolysis is the favored pathway over 1%Ru/SBA-15 catalyst. This was confirmed by the facts that CO_2 and benzene are main products over CeO_2 based catalysts, and CO

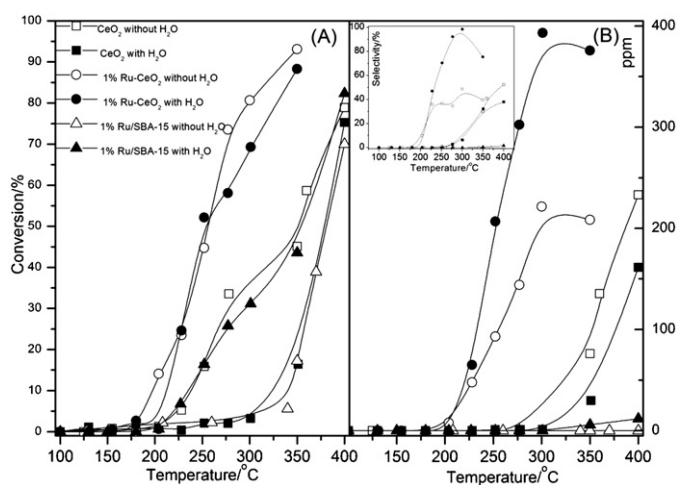


Fig. 6. Chlorobenzene conversion and selectivity to benzene as a function of the temperature. CB concentration: 550 ppm; Ar carrier, dry and water (~3%, v/v) conditions; GHSV: 15,000 h^{-1} .

is detected over 1%Ru/SBA-15 catalyst. Gonzalez-Velasco et al. found that the catalytic destruction of TCE was obviously improved in the presence of excess water due to the hydrolysis of TCE [31]. Bond and Rosa-Calzadilla et al. also reported that water, and not oxygen, was responsible for the conversion of CH_2Cl_2 and CCl_4 over Pt/ γ -alumina catalysts, through the aluminum hydroxyl groups [32].

Fig. 6(B) presents the selectivity to benzene over different catalysts under dry and humid Ar atmosphere. Except the 1%Ru/SBA-15 catalyst, pure CeO_2 and 1%Ru- CeO_2 catalysts both shows a higher selectivity to benzene, and the maximum value is between 30% and 100%, which is possibly ascribed to the easier dissociation of CB over CeO_2 and the plentiful surface hydroxyl groups. Moreover, it can be found that the selectivity to benzene over 1%Ru- CeO_2 catalyst under humid condition is evidently increased, even up to 100% at 300 °C. In contrast, the selectivity over pure CeO_2 catalyst is slightly inhibited in the present of water. There are the following three possible reasons: (1) the Ru can split water into OH and H [33]; (2) the Ru based catalysts is widely used in the WGS reaction [34,35]; (3) the Ru catalysts also are good hydrogenation or hydrodechlorination catalysts [36,37]. Additionally, it is considered that the likely reason of the poor selectivity to benzene over 1%Ru/SBA-15 catalyst is that CB destruction is only a pyrolysis process (under dry condition) or hydrolysis process (under humid condition). In order to further understand the importance of the supports, the catalytic activities of chlorobenzene and selectivity to benzene over 1%Ru/ Al_2O_3 , 1%Ru/ TiO_2 -rutile and 1%Ru/ TiO_2 -anatase catalysts under Ar and air conditions were investigated and presented in the Fig. 7. It can be seen from Fig. 7(A) that all three catalysts show a better catalytic activity for the CB oxidation under air atmosphere, but is far lower than that of 1%Ru- CeO_2 catalyst and slightly higher than that of 1%Ru/SBA-15 catalyst. Among the three catalysts, the 1%Ru/ TiO_2 -anatase shows the worst activity, which may be from the higher surface area and acidity of Al_2O_3 or the easier dispersion of Ru on the TiO_2 -rutile [38]. However, in the absence of gaseous oxygen, the CB conversion over these catalysts is very low and the maximum conversion is lower than 50% (1%Ru/ TiO_2 -rutile at 400 °C). Moreover, the selectivity to benzene over Ru supported Al_2O_3 and TiO_2 -rutile is always less than 10% and no more than 22% even over 1%Ru/ TiO_2 -anatase catalyst. The selectivity is much lower than that of CeO_2 based catalysts, but higher than 1%Ru/SBA-15 catalyst. These results show that the formation of benzene during CB catalytic destruction primarily depends on the essential properties of supports, such as the ability dissociating C–Cl bond or splitting water, surface hydroxyl groups and acidity.

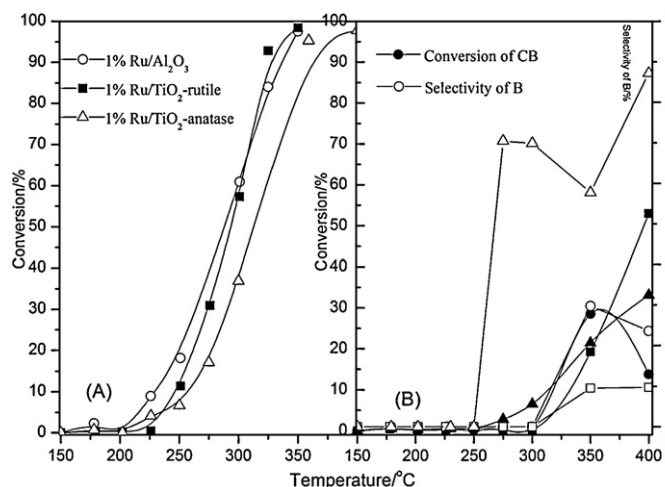


Fig. 7. Chlorobenzene conversion and selectivity to benzene as a function of the temperature over 1%Ru/Al₂O₃, 1%Ru/TiO₂-rutile and 1%Ru/TiO₂-anatase catalysts. CB concentration: 550 ppm; GHSV: 15,000 h⁻¹. (A) Air condition and (B) Ar condition.

According to the above results, it can be found that the formation of benzene is related with the following two factors: (1) the dissociation and dechlorination of CB; (2) the abundant surface hydroxyl groups as hydrogen source. Because CeO₂ based catalysts shows a good ability dissociating C–Cl bond and splitting water into OH and H, thus the higher selectivity to benzene can be obtained. Consequently, it can be speculated that the formation of monochlorobenzene (MCB) and benzene would be observed for 1,2-DCB catalytic decomposition over CeO₂ catalyst in absence of gaseous oxygen, and this speculation was confirmed by the following TPSR experiments (see Fig. 8).

Fig. 8 (left) presents the production of MCB and B under Ar atmosphere (before 140 min), and the starting temperature is about 280 °C. Notably, the formation of B (44 min) is later than MCB (40 min) and gradually disappears with the deactivation of CeO₂ catalyst (MCB can be observed during the whole test, but the yield decreases gradually), which shows the B is the product of MCB further dechlorination, not the direct dechlorination of 1,2-DCB.

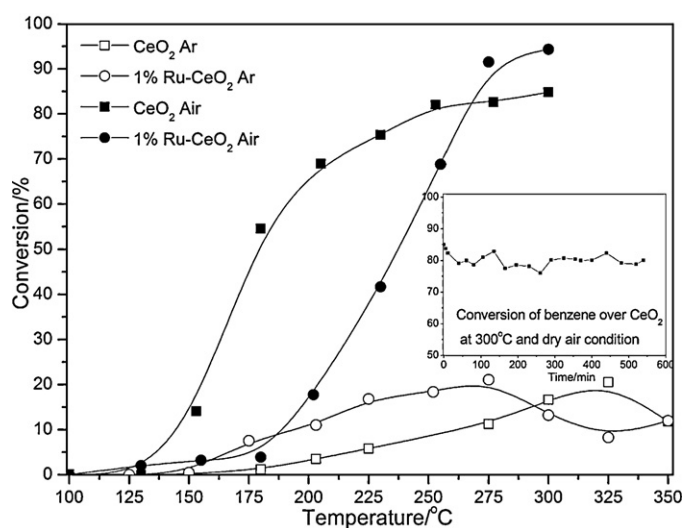


Fig. 9. Conversion of benzene over 1%Ru-CeO₂ and CeO₂ catalysts in absence and presence of O₂. Benzene concentration: 550 ppm; GHSV: 15,000 h⁻¹; catalyst amount: 200 mg.

After 10% oxygen is introduced, the conversion of 1,2-DCB rapidly increases to 94% (Fig. 8 (right, inset)) and a large amount of CO₂ is detected. Additionally, Cl₂ and trichlorobenzene (TCB) by-product can be detected only after 40 min and increases with the reaction time.

3.5. The effect of benzene and the formation of polychlorinated benzenes

In order to better understand the catalytic behavior of chlorobenzene over Ru doped CeO₂ catalysts, the catalytic oxidation of the intermediate species benzene over pure CeO₂ and 1%Ru-CeO₂ catalysts under Ar and air conditions is illustrated in Fig. 9. It is observed that the products originated from the oxidation of benzene are CO₂ and H₂O, there is no other organic compounds can be detected by GC and MS even in absence of oxygen (not shown). Pure CeO₂ catalyst shows an excellent catalytic performance in the

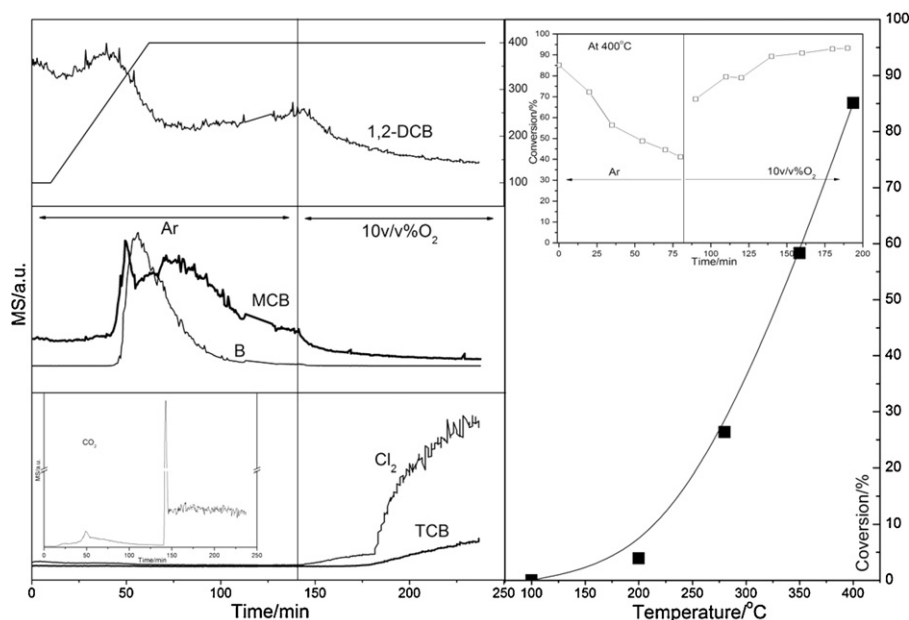


Fig. 8. TPSR and conversion profiles for 1,2-DCB decomposition over CeO₂ catalyst at 400 °C. 1,2-DCB concentration: 750 ppm; GHSV: 15,000 h⁻¹; catalyst amount: 200 mg.

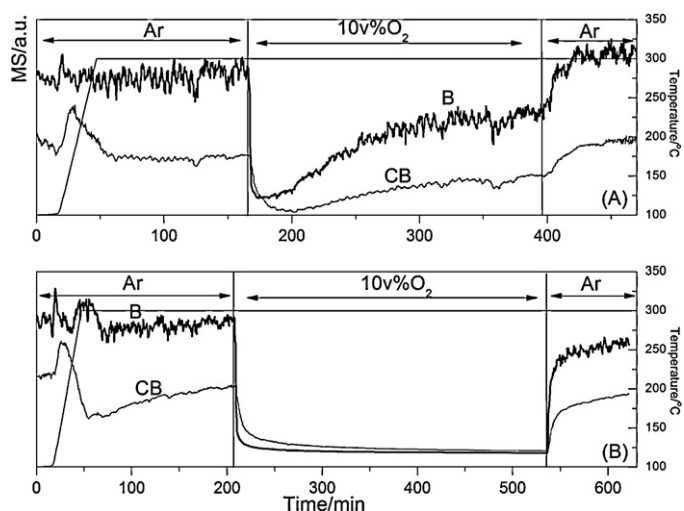


Fig. 10. TPSR profiles for the mixture of CB and benzene decomposition over CeO_2 (A) and 1%Ru- CeO_2 (B) catalysts at 300 °C. CB concentration: 750 ppm; benzene concentration: 750 ppm; GHSV: 15,000 h^{-1} ; catalyst amount: 200 mg.

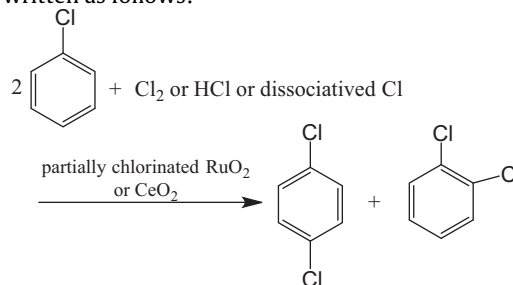
presence of oxygen, especially at lower temperature range, and the $T_{50\%}$ is only 180 °C. However, with the further increase of reaction temperature, the CeO_2 catalyst exhibits a gradual conversion curve and is not capable of achieving the complete oxidation of benzene even at 300 °C. In contrast, 1%Ru- CeO_2 catalyst is less active, but the 95% conversion of benzene can be achieved at 300 °C. In absence of oxygen, the pure CeO_2 and 1%Ru- CeO_2 catalysts both presents a very poor catalytic activity and the conversion is lower than 20% even at 350 °C due to the absence of surface active oxygen species, but 1%Ru- CeO_2 catalyst is slightly more active and different with that in the presence of oxygen probably due to the easier migration and evolution of the lattice oxygen. Comparing with Fig. 1, it can be found that the conversion of CB over pure CeO_2 and 1%Ru- CeO_2 catalysts is higher than the conversion of benzene both in the absence and presence of oxygen, which is attributed to the easier dissociation and split of C–Cl bond than C–H bond in the CB molecule [12]. Additionally, the pure CeO_2 catalyst was maintained under the combustion reaction at 300 °C and showed negligible change in activity over a time on stream of 10 h (see Fig. 9(inset)).

Fig. 10 shows the TPSR profiles of the binary mixtures of CB and benzene catalytic decomposition over CeO_2 and 1%Ru- CeO_2 catalysts, and is consistent with the results obtained via activity tests (Fig. 9). Notably, the deactivation of CB and benzene in the binary mixtures over pure CeO_2 catalyst is observed, but the activity of single benzene is stable (Fig. 9(inset)), which indicates that there possible is a common active site for CB and benzene catalytic oxidation. In our previous work [12], we found that the conversion of CB was obviously inhibited by the presence of benzene but the influence of CB on the conversion of benzene was negligible in binary mixtures of CB and benzene. Combining with the above experimental results, it can be inferred that the oxygen vacancy sites (are sites for gaseous oxygen adsorption, forming reactive oxygen species) may be the shared active sites for the deep oxidation of the adsorbed benzene (on oxygen vacancy, and surface OH or O^{2-}) and the dissociated CB on the $\text{Ce}^{3+}/\text{Ce}^{4+}$ sites. Due to the inhibition of the strongly adsorbed chlorine species on the oxygen adsorption centers [39], therefore the conversion of benzene also gradually drops accompanying with the deactivation of CeO_2 by CB in the binary mixtures of CB and benzene.

Although catalytic oxidation is one of the most promising technologies for the removal of chlorinated aromatics from waste gas, it was shown that the formation of polychlorinated benzenes is a serious drawback for the industrial application [40]. In our work,

1,4-DCB and 1,2-DCB dichlorinated by-products, no 1,3-DCB, are detected during TPSR experiments of pure CeO_2 catalyst (see Fig. 3 and Fig. 4) and stability tests of pure CeO_2 (see Fig. 5) and 1%Ru- CeO_2 catalyst (see reference [12]). It is worth noting that the formation of DCB just can be observed after the oxidation reaction lasts for at least 2 h. Additionally, 1,2,4-trichlorobenzene is formed in the case of 1,2-DCB catalytic combustion over pure CeO_2 catalyst. Well known, the formation of higher chlorinated compounds could be attributed to chlorination of chlorobenzene by Cl species (such as molecular chlorine, HCl or the Cl dissociatively adsorbed on the active sites) from the destruction of CB. The chlorination generally occurs through an aromatic electrophilic substitution mechanism and Lewis acids (such as FeCl_3 , AlCl_3 , SbCl_3 , MnCl_2 , MoCl_3 , SnCl_4 and TiCl_4) as catalysts, which would almost exclusively yield *para*- and *ortho*-dichlorobenzene [41]. Besides, the chlorination also occurs through a radical mechanism [42] and favors *meta*-dichlorobenzene. Therefore, it can be concluded that the formation of DCB by-products occurs via the electrophilic chlorination mechanism over CeO_2 based catalysts, and the partially chlorinated RuO_2 (RuO_xCl_y) or CeO_2 (CeO_xCl_y) [23] as Lewis acid catalysts promotes the chlorination reaction, which is verified indirectly by the fact that DCB is not detected over the fresh catalysts.

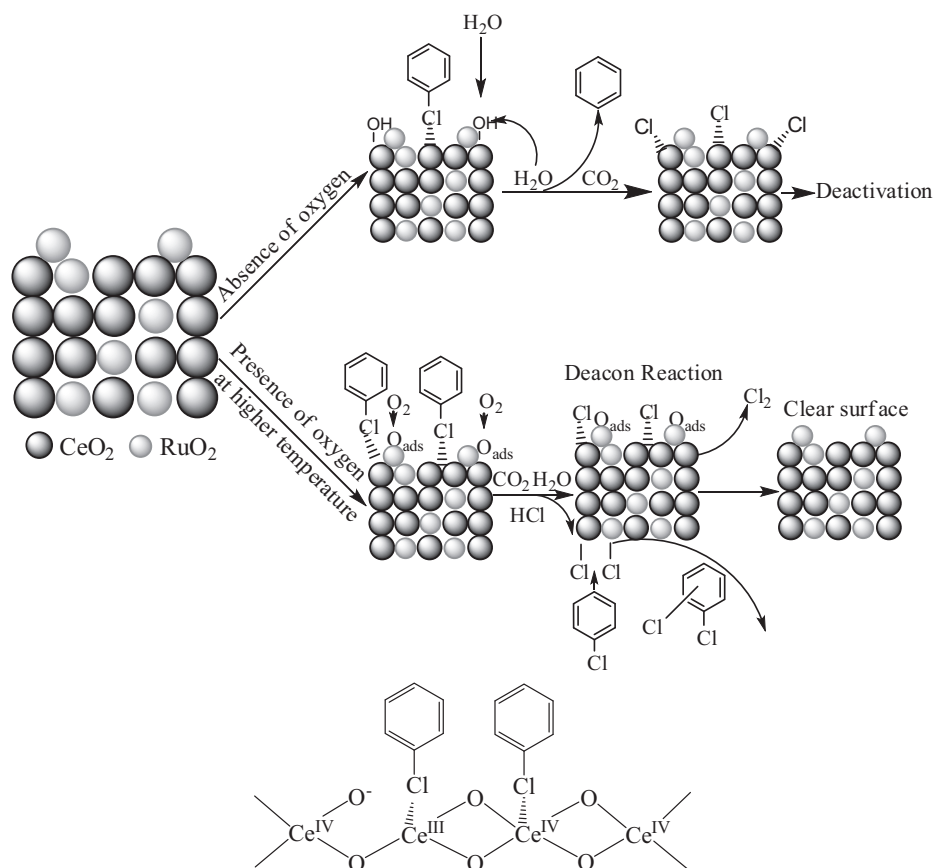
Thus the formation of 1,4 and 1,2-DCB over CeO_2 based catalysts can be written as follows:



3.6. Reaction mechanism for chlorobenzene oxidation over CeO_2 based catalysts

According to the above results and our previous works [12,15], catalytic combustion or destruction of chlorobenzene over pure CeO_2 and Ru doped CeO_2 catalysts can be summarized as follows:

- (1) CeO_2 presents high activity for catalytic destruction of CHCs, such as DCE, TCE and CB, which is attributed to the high dissociation ability for C–Cl bonds. However, the deactivation of CeO_2 is unavoidable and rapid due to the strong adsorption of the dissociated Cl species produced from the decomposition of CHCs on active sites.
- (2) The doping of Ru into CeO_2 slightly inhibits the activity of CeO_2 for CB catalytic combustion due to the blocking of the partial active sites, but the stability of catalysts can be improved distinctly, especially at lower temperature.
- (3) The better stability of the Ru doped CeO_2 catalysts can be ascribed to the Cl dissociatively adsorbed on active sites can be removed rapidly in form of Cl_2 via the Deacon process catalyzed by RuO_2 component.
- (4) Pure CeO_2 catalysts also show a better stability for the CB catalytic combustion at higher temperature (such as above 400 °C), due to the poor activity of CeO_2 for Deacon Reaction compared with RuO_2 .
- (5) In absence of oxygen, CeO_2 based catalysts still demonstrate evident activity and CO_2 is the main products except a small amount of benzene, which is ascribed to the abundant surface active oxygen and the easier migration of lattice oxygen in CeO_2 . In presence of oxygen, benzene would be an



Scheme 1. The proposed reaction mechanism for the catalytic combustion of CB over CeO_2 based catalysts.

intermediate species for the CB catalytic destruction and can be rapidly oxidized into CO_2 when the active oxygen species are sufficient.

- (6) The formation of benzene is attributed to the reaction of the phenyl groups from the dissociation of CB with the surface hydroxyl groups, and the presence of water in the feed can increase the selectivity of benzene, especially over Ru doped CeO_2 catalysts due to its higher splitting ability for H_2O and better hydrogenation activity.
- (7) The adsorption and dissociation of CB mainly occurs on $\text{Ce}^{3+}/\text{Ce}^{4+}$ active sites and benzene preferentially adsorbs on oxygen vacancy or O^{2-} or surface OH, and then the dissociated CB and benzene are completely oxidized into CO_2 and H_2O by the reactive oxygen species adsorbed on the oxygen vacancy sites.
- (8) 1,4-DCB and 1,2-DCB are the main by-products and formed via chlorination of chlorobenzene by the Cl species from the decomposition of CB, and the chlorination occurs through an aromatic electrophilic substitution mechanism. The partially chlorinated RuO_2 or CeO_2 as a Lewis acid catalyst promoted the production of polychlorinated benzenes.
- (9) The catalytic combustion of CB over CeO_2 based catalysts may occur via the following reaction pathways. Firstly, the CB is adsorbed and dissociated on $\text{Ce}^{3+}/\text{Ce}^{4+}$ (which can be facilitated with the help of $\text{Ce}^{3+}/\text{Ce}^{4+}$ as Lewis acid sites, and the CB molecule has a dipole moment) via nucleophilic attacks on the chlorine positions of the aromatic rings. Subsequently, the dissociated CB (phenyl groups) is completely oxidized into CO_2 by active oxygen species such as adsorbed oxygen or the migrated lattice oxygen via oxygen vacancies (in absence of gaseous oxygen). Simultaneously, the HCl and the

dissociatively adsorbed chlorine are oxidized into molecule chlorine by the surface reactive oxygen species on CeO_2 or RuO_2 (namely Deacon Reaction) and then removed from the $\text{Ce}^{3+}/\text{Ce}^{4+}$ active sites.

- (10) A plausible reaction mechanism can be proposed for the catalytic combustion of CB over CeO_2 based catalysts as shown in Scheme 1:

4. Conclusion

The catalytic combustion of CB over CeO_2 based catalysts was investigated in depth by TPSR technique and various supplementary experiments. The experiments in absence of oxygen showed that benzene is an intermediate product, which confirms the dissociation and splitting of C–Cl bond over $\text{Ce}^{3+}/\text{Ce}^{4+}$ active sites. The presence of water in the feed can inhibit the catalytic activity of CeO_2 based catalysts, which reflects the competition of the reactant molecules with water molecules for adsorption on the active sites. The dissociated CB (phenyl groups) can be rapidly oxidized into CO_2 and H_2O when the active oxygen species are sufficient. However, the chlorine dissociatively adsorbed on the active sites can result in the rapid deactivation of catalysts due to blocking or occupying the active sites. The better stability of the Ru- CeO_2 catalysts can be ascribed to the Cl dissociatively adsorbed on active sites can be removed rapidly in form of Cl_2 via the Deacon Reaction catalyzed by RuO_2 , and the importance of Deacon Reaction for improving the stability of catalysts is proved because the pure CeO_2 catalyst also presents a better stability at higher temperature (such as above 400°C). Additionally, the partial chlorination of RuO_2 or CeO_2 possibly occurs during the long reaction, which is responsible for the production of dichlorobenzene by-products.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2012.10.006>.

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